



Title: Quality Assurance and Quality Control Requirements for SW-846 Method 8330, Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)

WSC – CAM – VIII A

Quality Assurance and Quality Control Requirements for **SW-846 Method 8330,** **Nitroaromatics and Nitramines by High** **Performance Liquid Chromatography (HPLC)** for the Massachusetts Contingency Plan (MCP)

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VIII. High Performance Liquid Chromatography (HPLC) Methods

A. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for SW-846 Method 8330 Nitroaromatics and Nitramines by (HPLC)

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1.0 QA/QC Requirements for SW-846 Method 8330

1.1 Method Overview

SW-846 Method 8330 is primarily intended to be used for the trace analysis of explosive residues in water, soil, or sediment matrices using high performance liquid chromatography (HPLC) in tandem with a fixed 254 nm or variable-wavelength ultra-violet (UV) detector.

The Method provides a salting-out extraction procedure for low concentration (parts per trillion, or nanograms per liter) of explosives residues in surface or ground water; a direct injection method for diluted and filtered water samples with elevated concentrations; and an ultrasonic extraction procedure with acetonitrile for the analysis of soils and sediments.

1.1.1 Reporting Limits for SW-846 Method 8330

The reporting limit (RL) using SW-846 Method 8330 for an individual compound is dependent on the concentration of the lowest analytical standard in the initial calibration, choice of sample preparation/introduction method and percent (%) solids of the sample. Using an HPLC-system equipped with a pump capable of achieving 4000 psi, a 100 µl loop injector and a 254 nm UV detector, reporting limits should be approximately 250 - 1000 µg/kg (wet weight) for soil/sediment samples, based on the analysis of 2.0 grams of soil extracted in 10.0 ml of acetonitrile; 0.2 – 0.8 µg/L in aqueous samples using the low-level salting-out extraction method and 1000 - 1500 µg/kg (wet weight) for wastes (sample usually requires special pre-treatment and/or dilution prior to analysis). Reporting limits for SW-846 Method 8330 will be proportionately higher for samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

Somewhat lower limits may be achieved using a combination of HPLC coupled with thermospray-mass spectrometry (TS-MS) as described in SW-846 Method 8321A or a Gas Chromatograph-Electron Capture Detector (GC-ECD) system as described in Draft SW-846 Method 8095. At this time both of these methods are considered experimental and would require comprehensive Quality Control to demonstrate performance.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for Nitroaromatic compounds analyzed in support of MCP decision-making are presented in Appendix VIII A–1 of this document and Appendix VII-A, WSC-CAM-VIIA, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 Requirements of SW-846 Method 8330

Each laboratory that uses SW-846 Method 8330 is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the analysis of laboratory control spikes (LCSs) and LCS duplicates to assess



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analytical accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD) or matrix duplicates may also be used to evaluate precision when such samples are analyzed either at discretion of the laboratory or at the request of the data-user.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.5, Table VIII A-1 of this method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 method 8000B (Section 8.4). The data associated with the Initial Demonstration of Proficiency should be kept on file at the laboratory and made available to potential data-users on request. The data associated with the Initial Demonstration of Proficiency for SW-846 Method 8330 must include the following:

QC Element	Performance Criteria
Initial Calibration	WSC-CAM-VIII A, Table VIII A-1
Continuing Calibration	WSC-CAM-VIII A, Table VIII A-1
Method Blanks	WSC-CAM-VIII A, Table VIII A-1
Average Recovery	SW-846 Method 8000, Section 8.4
% Relative Standard Deviation	SW-846 Method 8000, Section 8.4
Surrogate Recovery*	WSC-CAM-VIII A, Table VIII A-1
Internal Standards	WSC-CAM-VIII A, Table VIII A-1
* Nitroaromatic and/or nitramine compounds not expected to be present in the sample.	

Note: Because of the extensive analyte list and number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to identify and correct the problem and repeat the analysis for all nonconforming analytes. All nonconforming analytes along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Proficiency data provided.

It is essential that laboratory-specific performance criteria for LCS, LCS duplicate and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table VIII A-1 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.



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For SW-846 Method 8330, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table VIII A-1. It should be noted that the performance standards listed in Table VIII A-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. In some cases, the standard laboratory acceptance criteria for the various QC elements may have to be modified to accommodate more rigorous project-specific data quality objectives prescribed by the data user. The laboratory may be required to modify routine sample introduction and/or analytical conditions to accommodate project-specific data quality objectives.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of high performance liquid chromatography, interpretation of chromatograms, experienced in the handling samples containing explosives and the analysis of explosive residues.

1.2 Summary of Method

SW-846 Method 8330 provides chromatographic and ultraviolet (UV) detection conditions for the identification and quantification of explosive residues introduced into the HPLC system. All positive measurements observed on the C-18 column (Reverse-phase HPLC column, 25 cm x 4.6 mm ID, 5 μ m particle size packing, Supelco LC-18, or equivalent) must be confirmed by injection under similar analytical conditions onto a dissimilar Reverse-phase HPLC column that achieves sufficient resolution of all the method target compounds.

Columns shown to demonstrate sufficient resolution with respect to a C-18 column in order of analytical performance include:

- (1) Reverse-phase HPLC column, 25 cm x 4.6 mm ID, 5 μ m particle size packing, Phenomenex Luna Phenyl-Hexyl;
- (2) Reverse-phase HPLC column, 25 cm x 4.6 mm ID, 5 μ m particle size packing, Phenomenex Synergi Polar-RP; and
- (3) CN column (Reverse-phase HPLC column, 25 cm x 4.6 mm ID, 5 μ m particle size packing, Supelco LC-CN, or equivalent).

Analytical Note: Column (3) is known to yield numerous co-elutions for the full list of target compounds proposed in this document.

1.2.1 Identification of Explosive Residues

Identification of target explosive residues is based on a coincidental retention time with a known standard using two-column confirmation. It should be noted that SW-846 method 8330 is particularly susceptible to severe co-elution problems when the detector is run at high sensitivity. Such co-elution problems affect the quantitation as well as identification of target analytes, and may result in poor agreement between quantitative results from two dissimilar columns. Therefore, even when the identification of target analytes has been confirmed on a dissimilar



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column, the analyst should evaluate the agreement of the quantitative results on both columns. Refer to SW-846 Method 8000, Section 7.10.4 regarding comparison of results from dissimilar columns. An RPD > 40% between dissimilar columns may indicate inadequate confirmation.

For some explosive residue analytes, their unique photo diode array (PDA) detector UV spectra or absorbance data using a different analytical (UV) wavelength may be used for confirmation. Depending on the concentration of the explosive residue, mass spectral (MS) confirmation or analysis using a dissimilar detector (GC/ECD) may also be a confirmation option.

1.2.2 Quantitation of Explosives, Explosive Residues and/or Metabolites

Quantitation of explosives, explosive residues and/or metabolites is accomplished by direct comparison of the peak height or area of the target analyte to the response of a known standard determined from a five-point calibration curve in appropriate units.

1.3 Sample Extraction/Cleanup Procedures

Samples for explosive residue analyses are normally prepared using one of the following methods prior to SW-846 Method 8330 analysis by HPLC.

Matrix	Method	SW-846 Method 8330 Section
Water - High Concentration	Direct Injection	2.3
Water - Low Concentration	Salting-Out with no evaporation	2.2
Water Pre-Concentration	Solid-Phase Extraction (SPE) using Porapak RDX, Sep-Pak, 6cc, 500mg	SW 846 Method 3535A (Modified) Jenkins et al., 1995 ^a
Soil/Sediment	Ultrasonic Extraction with Acetonitrile	2.4

a. Jenkins, T.F., P.G. Thorne, K.F., McCormick and Myers, E.F. (1995), Evaluation of clean solid phases for the extraction of nitroaromatics and nitrimines from water. U.S. Cold Regions Research and Engineering Laboratory, Hanover, NH, Special Report 95-16

SW-846 Method 3535A has been given preliminary approval for the analysis of aqueous samples. It allows for the use of SPE for the preparation of concentrated extracts from aqueous samples containing explosives, explosive residues and/or metabolites. This method has many advantages over the salting-out method, including speed, reproducibility, reduced solvent consumption and ease of use.

Analytical Note: There are no proven clean-up procedures for SW-846 Method 8330 extracts



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1.4 Method Interferences

1.4.1 Chemical Contaminants

Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences. Analyses of calibration and reagent blanks provide information about the presence of such contaminants. When potential interfering peaks are noted in blanks, the analyst should determine the cause of the contamination before reanalysis occurs. **Subtracting blank values from sample results is not permitted.** If the laboratory determines that the concentration reported in the blank is so high that false positive results are likely in the associated samples, then the laboratory should fully explain this situation in the case narrative.

1.4.2 Cross-contamination/Carryover

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of target or non-target compounds. After the analysis of a sample containing high concentrations of explosive residues, one or more blanks should be analyzed to check for potential cross-contamination/carryover. The concentration of explosive residue that can cause cross-contamination/carryover must be determined by the laboratory and will be dependent upon the concentration and level of saturation of the particular analyte. Concentrations of explosive residues which exceed the highest point of calibration curve should prompt the analyst to check for potential cross-contamination/carryover. In addition, samples containing non-target, chromatographically recalcitrant compounds may also present potential for cross-contamination/carryover. Laboratories should be aware that carryover from highly-retained compounds may not appear until a later sample run.

1.4.3 Photodegradation

To the extent practical, never expose samples for explosive residue analysis to direct sunlight.

1.4.4 Other Potential Analytical Interferences

2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of approximately 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain Tetryl should be diluted with acetonitrile prior to filtration and acidified to pH <3. In addition, any sample expected to contain Tetryl should not be exposed to temperatures above room temperature.



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Degradation products of Tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak heights rather than peak areas should be used when Tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

Methanol must be used as an extraction solvent whenever HMX is a target analyte and high-level direct injection analytical procedure is utilized.

1.5 Quality Control Requirements for SW-846 Method 8330

1.5.1 General Quality Control Requirements for Determinative Chromatographic Methods

It should be noted that if any of the method-specific chromatographic performance standards are not met, the analyst should examine the HPLC system for leaks, proper pressure delivery, and/or a dirty guard column. Diligent maintenance and continuous monitoring of HPLC system performance is an essential component of data quality. Refer to SW-846 Method 8000, Section 3.6 for specific HPLC maintenance and corrective action information.

Refer to SW-846 Method 8000, Section 7.0 for general quality control procedures for all chromatographic methods, including SW-846 Method 8330. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all chromatographic data.

Quality Control procedures necessary to evaluate the HPLC system operation, including evaluation of retention time windows, calibration verification and chromatographic analysis of samples may be found in Method 8000, Sec. 7.0.

1.5.2 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8330

Specific QA/QC requirements and performance standards for SW-846 Method 8330 are presented in Table VIII A-1. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide an LSP with "Presumptive Certainty" regarding the usability of analytical data to support MCP decisions. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty", parties must:

- (a) Comply with the procedures described and referenced in WSC-CAM-VIII A;
- (b) Comply with the applicable QC analytical requirements prescribed in Table VIII A-1 for this test procedure;
- (c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table VIII A-1 for this test method; and



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(d) Adopt the reporting formats and elements specified in the CAM

In achieving “Presumptive Certainty” status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;
- ✓ May be used in a data usability assessment, and, if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered usable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to support a data representativeness assessment

Widespread adherence to the “Presumptive Certainty” approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the “Presumptive Certainty” option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

1.5.3 Soil/Sediment Sample Homogenization

Soil and sediment samples must be thoroughly homogenized prior to analysis by SW-846 Method 8330. Dry soil samples in air at room temperature or colder to a constant weight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile-rinsed mortar to pass a 30-mesh sieve.

NOTE: When elevated levels of explosive residue are expected, soil samples should be screened by SW-846 Method 8515 prior to grinding in a mortar and pestle (See safety precautions in Section 11.2 of the method) and Section 3.3.



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Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new HPLC column is installed. (2) Calculated according to the method. (Section 7.6 of SW-846 8000).	No	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Minimum of 5 standards. (2) Individual solvent blanks (acetonitrile, methanol and water) must be run prior to preparation of stock standards (3) Low standard must be \leq reporting limit. (4) %RSD should be ≤ 20 or "r" should be ≥ 0.995 . (5) If regression analysis is used, the curve may be forced through the origin. (6) Curves must be verified by an independent ICV before analysis.	No	Recalibrate as required by method.	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds in case narrative. If the average response factor or linear regression are not used for analyte quantitation (e.g., use of a quadratic equation), this must be noted in the case narrative with a list of the affected analytes..
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Prior to samples, after every 10 samples, and at the end of the analytical sequence. (2) Concentration level near midpoint of curve. (3) Percent difference or percent drift of calibration factors should be ≤ 15 . (4) Verify all analytes fall within retention time windows.	No	(1) Perform instrument maintenance, reanalyze CCAL and/or recalibrate as required by method. (2) Reanalyze "associated samples" if beginning or closing CCAL exhibited low response and associated analytes were or were not detected in samples. (3) Reanalyze "associated samples" if beginning or closing CCAL exhibited high response and associated analytes were detected in the samples. NOTE: "Associated Samples" refers to all samples analyzed since the last acceptable CCAL.	Report exceedances in case narrative.



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Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil). (3) Target analytes must be less than or equal to reporting limit.	Yes	Locate source of contamination; correct problem; re-extract associated samples if contaminants are present in the method blank.	(1) Report non-conformances in case narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention (such as the case narrative), should qualify the sample results. (3) If re-extraction is performed within holding time, the laboratory may report results of the re-extraction only. (4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.
Laboratory Control Spikes (LCSs)	Laboratory Method Accuracy	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level should be between low and mid-level standard. (4) Must contain all target analytes. (5) Matrix-specific (e.g., soil, water). (6) Percent recoveries must be between 60-120 for soils and 70-110 for waters. (7) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above.	Yes	Recalculate the percent recoveries. Check MS/MSD; if recoveries are acceptable in MS/MSD, nonconformance may be isolated to LCS. If recoveries are outside criteria in MS/MSD, re-extract associated samples and/or narrate nonconformances.	(1) Report non-conformances in Environmental Laboratory case narrative. (2) If re-extraction is performed within holding time, the laboratory may report results of the re-extraction only. (3) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction. (4) Individual laboratories must identify and document "difficult" (**) analytes for which laboratory-determined recovery ranges routinely exceed the 60-120 for soils and 70-110 for waters criterion. Exceedances for these "difficult" analytes must be qualified in Environmental Laboratory case narrative. Analytical data to support the "difficult" analyte classification must be available for review during an audit.



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Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
LCS Duplicate	Laboratory Method Precision	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using same standard source and concentration as LCS. (3) Must contain all target analytes. (4) Recommended to be run immediately after LCS in analytical sequence. (5) Laboratory-determined percent recoveries must be between 60-120 for soils and 70-110 for waters. (6) Matrix-specific (e.g., soil, water). (7) Laboratory-determined Relative Percent Difference (RPD) must be ≤ 25 except for "difficult" (**) analytes which must be ≤ 50 .	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Individual laboratories must identify and document "difficult" (**) analytes for which laboratory-determined RPDs routinely exceed the ≤ 25 criterion. (3) Exceedances for these "difficult" analytes must be qualified in Environmental Laboratory case narrative. Analytical data to support the "difficult" analyte classification must be available for review during an audit. (4) Narrate non-conformances
MS/MSDs	Method Accuracy in Sample Matrix Method Precision in Sample Matrix	(1) Extracted with every 20 samples at discretion of laboratory or at request of data user. (2) Matrix-specific. (3) Prepared using standard source different than that used for initial calibration. (4) Concentration level should be between low and mid-level standard. (5) Must contain all target analytes. (6) Percent recoveries should be between 60-120 for soils and 70-110 for waters. (7) RPDs should be ≤ 30 .	Yes (Only when requested by the data-user)	Check LCS; if recoveries acceptable in LCS, narrate nonconformance.	Report exceedances in the Environmental Laboratory case narrative..



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Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Surrogates	Accuracy in Sample Matrix	(1) Recommended surrogate (1 minimum): 1,2-Dinitrobenzene (2) Percent recovery must be between 70 - 110 for surrogates on both columns. (3) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above.	Yes (report surrogate recoveries from both columns)	If the surrogate is outside limits on both columns, re-extract the sample. If the surrogate is outside limits on one column only, re-analyze the sample. If a surrogate is diluted to a concentration below that of the lowest calibration standard, no corrective action is necessary.	(1) Report exceedances in case narrative. (2) If re-extraction or reanalysis yields similar surrogate nonconformances, the laboratory should report results of both extractions or analyses. (3) If re-extraction or reanalysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the re-extraction or reanalysis only. (4) If re-extraction or reanalysis is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial and re-extraction or reanalysis. (5) If sample is not re-extracted or reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
Internal Standards <i>(Optional)</i>	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Recommended internal standard (1 minimum): 3,4-Dinitrotoluene (2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard. (3) Retention times of internal standards must be within ± 30 seconds of retention times in associated continuing calibration standard	No	If internal standard is outside limits, reanalyze sample unless obvious interference present.	(1) Report exceedances in case narrative. (2) If reanalysis yields similar internal standard nonconformance, the laboratory should report both results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recovery, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time and yields acceptable internal standard recovery, the laboratory must report results of both analyses. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.



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Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Identification and Quantitation	Inter-laboratory consistency	(1) Laboratory should use the average calibration factor of each analyte or the linear regression curve for quantitation. (2) Secondary column analysis: Laboratory must utilize a C-18 reverse phase HPLC column for the primary analysis and a CN reverse phase HPLC column for confirmation of positive results. The laboratory must report the results from the C-18 column unless obvious interference is present. In this case, the laboratory should report and narrate the CN column result. All required QA/QC parameters (e.g., calibrations, LCSs, etc.) must be met on the secondary column as well. (3) Peak heights instead of peak areas must be used for quantitation when tetraol is present in concentrations that are significant relative to the concentrations of 2,4,6-trinitrotoluene.	No	NA	(1) If the RPD between the dual column results exceeds 40, the laboratory should qualify the sample results and/or note the exceedance in the case narrative. <u>NOTE:</u> If the high RPD can be definitively attributed to interference on one of the two columns, the laboratory should report the lower value and provide a discussion in the case narrative that this approach was employed. (2) If the average response factor or linear regression are not used for analyte quantitation (e.g. quadratic equation), this must be noted in the case narrative with a list of the affected analytes.
General Reporting Issues	NA	(1) The laboratory must report values \geq the sample-specific reporting limit; optionally, values below the sample-specific reporting limit can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the <u>lowest</u> dilution within the valid calibration range for <u>each</u> analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported.	Yes	NA	Qualification of the data is required if reporting values below the sample-specific reporting limit.

HPLC = High Performance Liquid Chromatography
RPDs = Relative Percent Differences

MS/MSDs = Matrix Spikes/Matrix Spike Duplicates
%RSD = Percent Relative Standard Deviation

"r" = Correlation Coefficient
ICV = Initial Calibration Verification – separate source standard



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1.6 MCP Analyte List for SW-846 Method 8330

The MCP analyte list for SW-846 Method 8330, presented in Table VIII A-2, is intended to be protective of human health and the environment. The analyte list is comprised of sixteen (16) nitroaromatic and nitroamine compounds that are routinely encountered at locations impacted by military ordnance (artillery target areas, demolition ranges, etc.) and are readily analyzable by SW-846 Method 8330. The analyte list contains both high explosive residues and the environmental metabolites of trinitrotoluene (TNT). These compounds, with the exception of 2,6-Diamino-4-nitrotoluene and 2,4-Diamino-6-nitrotoluene (two additional environmental metabolites of TNT), are specifically identified as explosive residue analytes in Section 1 of SW-846 Method 8330.

Of the listed SW-846 Method 8330 analytes, only HMX, RDX, and 2,4-Dinitrotoluene have promulgated or proposed compound-specific MCP Method 1 Groundwater/Soil Standards as described in 310 CMR 40.0974 and 40.0980, respectively. The remaining analytes, with the exception of the four (4) TNT environmental metabolites (4-Am-DNT, 2-Am-DNT, 2,6-DAM-4NT and 2,4-DAM-6NT), have compound-specific Reportable Concentrations (RC) as described in 310 CMR 40.0360 and 40.1600. Of the analytes without a proposed or promulgated MCP Method 1 Standard, only Tetryl, the three (3) Nitrotoluene isomers and the four (4) TNT environmental metabolites do not have sufficient toxicity information at this time for the Department (or others) to develop compound-specific MCP Method 2 Standards for groundwaters and soils, as described in 310 CMR 40.0980.

The MCP Method 1 Groundwater/Soil Standards used to characterize the risk of harm posed by oil or hazardous materials at a disposal site are described in 310 CMR 40.0974(2), Table 1. This list of groundwater/soil standards, developed by the Department, takes into account a defined set of conservative potential exposure pathways likely to be encountered at most disposal sites. Method 1 Standards have been developed by the Department for over one hundred organic and inorganic contaminants that are commonly encountered at disposal sites. The MCP Method 1 Groundwater/Soil Standards list is periodically reviewed and updated by the Department. When compounds are added to the MCP Method 1 Groundwater/Soil Standards list that are suitable for analysis by SW-846 Method 8330, the analyte list for this method will be updated accordingly.

MCP Method 2 Groundwater/Soil Standards are developed by the Department (or others) for contaminants of concern for which MCP Method 1 Standards have not been promulgated. The use of Department-developed MCP Method 2 Standards is discretionary. Alternatively, site-specific MCP Method 2 Standards may be developed or a Method 3 risk characterization, as described in 310 CMR 40.0990, may be conducted to evaluate or characterize the risk of harm posed by oil or hazardous materials at a disposal site. An updated list of the Department-derived MCP Method 2 Standards may be found at the following URL:

<http://www.mass.gov/dep/cleanup/laws/method2.htm>

1.6.1 Additional SW-846 Method 8330 Analytically Amenable Compounds

SW-846 Method 8330 may also be utilized for the determination of additional nitroaromatic and nitroamine explosive compounds not specifically identified as explosive residue analytes in Section 1 of SW-846 Method 8330. These additional analytes, shown as "Additional Analytically Amenable Compounds" in Table VIII A-2 include, but are not limited to, PETN, Nitroglycerine, and Picric Acid. These compounds are mentioned in this guidance for informational purposes only and need only



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be evaluated at MCP disposal sites that have known or suspected impacts by these additional compounds. Of these three (3) Analytically Amenable Compounds only PETN does not have an MCP Reportable Concentration.

1.7 Additional Analyte Reporting Requirements for SW-846 Method 8330

While it is not necessary to request and report all the SW-846 Method 8330 analytes listed in Table VIII A-2 to obtain "Presumptive Certainty" status, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP strongly recommends use of the full SW-846 Method 8330 analyte list, including the four (4) TNT metabolites, when previously uncharacterized ordnance-impacted sites with unknown or complex history and/or disposal practices are characterized for explosive residue analytes. These assessment activities include but are not limited to:

- ✓ Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- ✓ Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- ✓ Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- ✓ Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In a limited number of cases, the use of the full SW-846 Method 8330 analyte list may not be warranted for ordnance-impacted sites, with respect to the aforementioned data representativeness concerns. These circumstances include:

- ✓ Uncharacterized sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or
- ✓ Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

Note that a desire to avoid detection and quantitation of a contaminant that is present or likely present at a site above background levels is not a valid reason to limit an analyte list, and that such an action could constitute a criminal violation of MGL c. 21E.

In cases where a truncated list of method analytes is selected, laboratories must still employ the method-specific quality control requirements and performance standards associated with the requested analytes list to obtain "Presumptive Certainty" status.

The Reporting Limit (based on the concentration of the lowest calibration standard) for each contaminant of concern must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 2 Standards, RfDs, benchmark values, background, etc.). Meeting "MCP program" reporting limits may require analytical modifications, such as increased sampling weight or volume to increase sensitivity. All such modifications must be described in the Environmental Laboratory case narrative.



Title: SW-846 Method 8330 Analyte List

Analyte	CASN	MCP REPORTABLE CONCENTRATIONS UNLESS OTHERWISE SPECIFIED	
		RC-GW-1	RC-S-1
		mg/L (ppm)	µg/g (ppm)
HMX ^a	2691410	0.2 ¹	2 ¹
RDX (Cyclonite) ^{2, 3, b}	121824	1	100
1,3,5-Trinitrobenzene (1,3,5-TNB) ⁴	99354	0.5	50
1,3-Dinitrobenzene (1,3-DNB) ⁴	99650	1	100
Nitrobenzene (NB) ⁴	98953	5	500
Tetryl ^c	479458	1	100
2,4,6-Trinitrotoluene (TNT) ⁴	118967	1	100
4-Amino-2, 6-dinitrotoluene (4 – Am – DNT)	1946510	Not Promulgated	Not Promulgated
2-Amino-4, 6-dinitrotoluene (2 – Am -DNT)	35572782	Not Promulgated	Not Promulgated
2,6-Diamino-4-nitrotoluene (2,6-DAm-4NT)	59299753	Not Promulgated	Not Promulgated
2,4-Diamino-6-nitrotoluene (2,4-DAm-6NT)	6629294	Not Promulgated	Not Promulgated
2,6-Dinitrotoluene (2,6-DNT) ⁴	606202	1	100
2,4-Dinitrotoluene (2,4-DNT) ⁴	121142	0.03 ⁵	0.7 ⁶
2-Nitrotoluene (2-NT)	88722	5	500
4-Nitrotoluene (4-NT)	99990	5	500
3-Nitrotoluene (3-NT)	99081	5	500
Additional Analytically Amenable Compounds:			
Nitroglycerin	55630	0.5	50
PETN ^d	78115	Not Promulgated	Not Promulgated
Picric Acid (Trinitrophenol)	88891	1	100

1 = Proposed MCP Method 1 Numerical Standard (20 December 2001)

2 = **RDX** is identified as Cyclonite in Subpart P, the Massachusetts Oil and hazardous Materials List (MOHML)

3 = Proposed MCP Method 1 Numerical Standard (20 December 2001) for RDX:

GW-1 = 0.8 ppb.,; GW-1 & S-1 = 1 mg/kg

4 = Department developed Method 2 Standard available. Use of these Standards discretionary. Numerical values for these compounds may be found at:

<http://Mass.Gov/dep/cleanup/laws/method2.htm>

5 = Method 1 GW-1 Standard

6 = Method 1 GW-1 & S-1 Standard

a = **HMX** = Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

b = **RDX** = Hexahydro-1,3,5-trinitro-1,3,5-triazine

c = **Tetryl** = Methyl-2,4,6-trinitrophenylnitramine

d = **PETN** = Pentaerythritol tetranitrate



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2.0 Data Usability Assessment for SW-846 Method 8330

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for SW-846 Method 8330 which may be used to assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document

3.0 Reporting Requirements for SW-846 Method 8330

3.1 General Reporting Requirements for SW-846 Method 8330

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in CAM-VII A, Section 2.4. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including:

- Laboratory identification information presented in WSC-CAM - VII A, Section 2.4.1,
- Analytical results and supporting information in WSC-CAM - VII A, Section 2.4.2,
- Sample- and batch-specific QC information in WSC-CAM - VII A, Section 2.4.3,
- Laboratory Report Certification Statement in WSC-CAM - VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in WSC-CAM - VII A, Exhibit VII A-1,
- Environmental Laboratory Case Narrative contents in WSC-CAM - VII A, Section 2.4.5,
- Chain of Custody Form requirements in WSC-CAM - VII A, Section 2.4.6

3.2 Specific Reporting Requirements for SW-846 Method 8330

Specific Quality Control Requirements and Performance Standards for SW-846 Method 8330 are presented in Table VIII A-1. Specific reporting requirements for SW-846 Method 8330 are summarized below in Table VIII A-3 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis.



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Table VIII A-3 Routine Reporting Requirements for SW-846 Method 8330

Parameter	Required Analytical Deliverable
Initial Calibration	NO
Continuing Calibration (CCAL)	NO
Method (Preparation) Blank	YES
Laboratory Control Spikes (LCSs)	YES
LCS Duplicate	YES
Matrix Spike (MS)	YES (if requested field MS)
Matrix Spike Duplicate (MSD)	YES (if requested field MS/MSD)
Field Matrix Duplicate (MD)	YES (if requested by Data User)
Surrogates	YES
Internal Standards (ISs)	NO
Identification and Quantification	NO
General Reporting Issues	YES

3.3 Special Analytical Safety Precautions

Standard precautionary measures used for handling other organic compounds should be sufficient in most circumstances for the safe handling of the analytes targeted by SW-846 Method 8330. Special caution should be exercised when handling any neat material (if used to prepare analytical standards) or in the rare case that soil, sediment or waste samples are highly contaminated (greater than 1,000 mg/kg on a dry weight basis) with explosives.

Soil and sediment samples should be air dried at room temperature (or lower) only. See Section 1.5.3.

It is advisable to screen soil or waste samples using SW-846 Method 8515 to determine whether high concentrations of explosives are present. This screening method is most sensitive for 2,4,6-TNT, the analyte most often detected in high concentrations in soil samples, however, other nitroaromatics will also cause a color to be developed that will provide a rough estimation of their concentrations. **Highly contaminated soil or sediment samples should never be ground in a mortar and pestle.**

Visual examination of a soil or sediment sample is also important when the sample is taken from a site expected to contain explosives. Lumps of material with explosive-like appearance should be considered suspect and never ground manually. Explosives are generally a very finely ground grayish-white material.



Title: Sample Collection, Preservation, And Handling Procedures for SW-846 Method 8330,
Including Table VIII A-4

General Sampling Precautions and Safety Alerts

Sampling of media potentially contaminated with explosives should only occur after appropriate safety level clearance of the sampling site. High explosives such as RDX, HMX and TNT have chemical, physical and toxicological properties different from environmental contaminants routinely encountered at MCP sites. **The potential for explosion requires that due caution be exercised when planning and implementing field activities at sites where these materials are expected to be present (at % level concentrations). As a final caution, unexploded ordnance (UXO) may be encountered on the surface or buried in the soil at many military ranges.**

Detailed procedures for sample collection, preservation, and handling of field samples for Organic Analyses are presented in SW-846, Chapter 4.0. Sampling procedures, containers and preservation techniques for explosive residue analyses are similar to those used for semi-volatile analyses. Containers used to collect samples for the determination of explosive residues should be water washed followed by methanol (or isopropanol) rinsing (see Sec. 4.1.4 for specific instructions on glassware cleaning). The sample containers should be of glass or Teflon, and have screw-caps with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. However, acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may **never** be used for the storage of samples for explosive residue analyses due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g. if an automatic sampler is used), run organic-free reagent water through the sampler and use as a field blank.

To the extent practical, never expose samples for explosive residue analysis to direct sunlight.

Safety Alert

After a sampling location has been cleared by the Site Safety Officer to the appropriate safety level, sampling of potentially contaminated media for explosive residues may proceed. Active and inactive sites with a history of energetic materials (EM) use or disposal should be cleared for both residual explosives and Unexploded Ordnance (UXO).

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for explosive residue compounds analyzed in support of MCP decision-making are summarized below in Table VIII A-4 and presented in Appendix VII-A of WSC-CAM-VIIA, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".



Title: Sample Collection, Preservation, And Handling Procedures for SW-846 Method 8330, Including
Table VIII A-4 (*continued*)

Table VIII A-4 Containers, Preservation and Hold Times for Explosive Residue Analyses

Sample Matrix	Container	Preservation	Holding Time
Concentrated Waste Samples	125 mL wide mouth glass with Teflon-lined cap	None Required	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction
Aqueous Samples ¹	1-Liter amber glass bottle with Teflon-lined screw cap	Stored in dark Cool to 4°C Acidify to pH 2.0 w/ NaHSO ₄ (1.2 g/L)	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction
Soil/Sediments ^{2,3}	16-oz. (500 mL) wide-mouthed amber glass jar with Teflon-lined screw cap	Store in dark Cool to 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction

1. For aqueous samples with a chlorine residual, add 1-mL 10% sodium thiosulfate solution per container (or 0.008%). Addition of thiosulfate solution to sample container may be performed in the laboratory prior to field use.
2. Soil samples that have been frozen within 24 hours of collection may be held for up to eight (8) weeks prior to analysis.
3. Soil samples contaminated with explosive residues are notoriously heterogeneous. Samples should be homogenized prior to analysis. (**See previous precaution!**)